Preparation of Mono- and Bis(germyl)nitrilimines from Germylenes and Stannyl Diazo Derivatives

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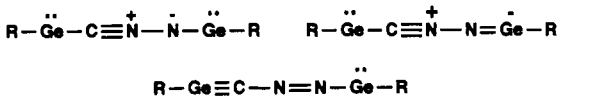
Summary: (Silyl)(germyl)- and bis(germyl)nitrilimines ***2*** *and* ***5*** *are obtained by adding [bis(trimethylsilyl)methyl](pentamethylcyclopentadienyl)germylene (1) to (triisopropylsilyl)(trimethylstannyl)diazomethane and bis(trimethylstannyl)diazomethane, respectively; the reaction mechanism is discussed.*

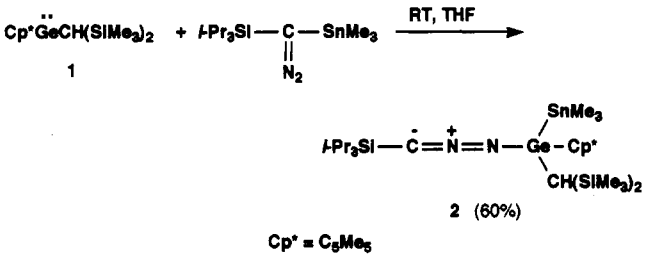
In the last few years, we have shown that, using the right set of substituents, nitrilimines can exist as stable compounds at room temperature.[1] Nitrilimines have a bent allenic structure,[2] except those possessing substituents with accessible vacant orbitals. In the latter case, nitrilimines have a propargylic type structure,[3,4] and the interaction of the CNN skeleton with the heteroatom substituents induces a shortening of the heteroatom–nitrogen or heteroatom–carbon bond lengths compared to classical single bonds; the *N*-phosphonio-[3a] and *C*-borylnitrilimines[3b] are typical examples. Therefore, it was tempting to prepare nitrilimines featuring germanediyl moieties, in order to study the multiple-bond character of the nitrogen– or/and carbon–germanium bond (Chart 1). Stannyl diazo derivatives react with a variety of electrophiles, leading to nitrilimines.[2b,5] On the other hand, pentamethylcyclopentadienyl (Cp*) substituted germylenes are known to undergo nucleophilic substitutions.[6] Here we report the surprising results observed in the reaction of [bis(trimethylsilyl)methyl](pentamethylcyclopentadienyl)germylene (**1**)[6a] with (triisopropylsilyl)(trimethylstannyl)diazomethane[5] and bis(trimethylstannyl)diazomethane.[7]

(Triisopropylsilyl)(trimethylstannyl)diazomethane reacted at room temperature in a THF solution with 1 equiv of **1**, leading, after workup, to a pale yellow oil identified as a nitrilimine[8] on the basis of ^{14}N NMR (δ −183 (*C*N*N*))[9] and ^{13}C NMR (δ 49.85 (*C*NN)) data and the strong and broad absorption in the IR spectrum at 2076 cm^{-1}.

Chart 1



Scheme 1



Surprisingly, NMR data also revealed the presence of a trimethylstannyl group (^{1}H NMR δ 0.48 ($J_{^{117}SnH}$ = 47.2 Hz, $J_{^{119}SnH}$ = 49.2 Hz, 9 H); ^{13}C NMR δ −4.28 ($J_{^{117}SnH}$ = 244.2 Hz, $J_{^{119}SnH}$ = 255.6 Hz); ^{119}Sn NMR δ −77.88) and also a fluxional Cp* substituent (^{1}H NMR δ 1.85 (15 H);

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(8) **2**: Neat (triisopropylsilyl)(trimethylstannyl)diazomethane (0.824 g, 2.3 mmol) was added at room temperature to a THF solution (5 mL) of **1** (0.838 g, 2.3 mmol). After the mixture was stirred for 1.5 h at room temperature, the solvent was removed under vacuum. The pale yellow oily nitrilimine **2** was washed three times with acetonitrile (5 mL) and dried in vacuo (1.00 g, 60% yield): bp 104 °C (5 × 10^{-2} mmHg); ^{1}H NMR (C_6D_6) δ −0.07, −0.06 (s, 1 H, C*H*SiCH$_3$), 0.13, 0.39 (s, 18 H, SiC*H*$_3$), 0.48 (s, $J_{^{117}SnH}$ = 47.2 Hz, $J_{^{119}SnH}$ = 49.2 Hz, 9 H, SnC*H*$_3$), 1.08 (m, 21 H, SiC*H*CH$_3$), 1.85 (broad s, 15 H, CpC*H*$_3$); ^{13}C NMR (C_6D_6) δ −4.28 (s, $J_{^{117}SnC}$ = 244.2 Hz, $J_{^{119}SnC}$ = 255.6 Hz, SnCH$_3$), 3.94, 4.72 (s, SiCH$_3$), 12.92 (s, SiCHCH$_3$), 13.20 (broad s, CpCH$_3$), 19.21 (s, SiCHCH$_3$), 49.85 (s, CNN), 135.56 (broad s, Cp), CHSiCH$_3$ was not observed, probably hidden by SiCH$_3$; ^{14}N NMR (C_6D_6) δ −183 ($\nu_{1/2}$ = 240 Hz, CNN); ^{119}Sn NMR (C_6D_6) δ −77.88; ^{29}Si NMR (C_6D_6) δ −0.6, −0.1, 0.9; IR (THF, ν (cm^{-1})) 2076 (CNN). Anal. Calcd for $C_{30}H_{64}GeN_2Si_3Sn$: C, 49.46; H, 8.85; N, 3.84. Found: C, 49.49; H, 8.80; N, 3.79. **5**: The mixture of diastereomeric nitrilimines **5** was obtained as a pale yellow powder from a saturated THF solution at −80 °C (48% yield): ^{1}H NMR (C_6D_6) δ = −0.57, −0.55, −0.47, −0.45 (s, 2 H, C*H*SiCH$_3$), 0.05, 0.12 (s, 18 H, SiC*H*$_3$), 0.37, 0.38 (s, $J_{^{117}SnH}$ = 46.1 Hz, $J_{^{119}SnH}$ = 48.2 Hz, 9 H, SnC*H*$_3$), 0.45, 0.52 (s, 18 H, SiC*H*$_3$), 0.63, 0.64 (s, $J_{^{117}SnH}$ = 46.2 Hz, $J_{^{119}SnH}$ = 48.1 Hz, 9 H, SnC*H*$_3$), 1.79 (broad s, 15 H, CpC*H*$_3$), 1.90 (broad s, 15 H, CpC*H*$_3$); ^{13}C NMR (C_7D_8) δ −5.22 (s, $J_{^{117}SnC}$ = 250.1 Hz, $J_{^{119}SnC}$ = 264.6 Hz, SnCH$_3$), −4.28 (s, $J_{^{117}SnC}$ = 234.8 Hz, $J_{^{119}SnC}$ = 244.5 Hz, SnCH$_3$), 3.14, 3.44, 3.78, 4.90 (s, SiCH$_3$), 12.40 (broad s, CpCH$_3$), 63.71 (s, CNN), 135.01 (broad s, Cp), CHSiCH$_3$ was not observed, probably hidden by SiCH$_3$; ^{14}N NMR (C_7D_8) δ = −173 ($\nu_{1/2}$ = 250 Hz, CNN); ^{119}Sn NMR (C_6D_6) δ −83.12, −81.77, −67.09, −66.44; IR (ether, ν (cm^{-1})) 2052 (CNN). Anal. Calcd for $C_{41}H_{86}Ge_2N_2Si_4Sn_2$: C, 44.69; H, 7.87; N, 2.54. Found: C, 44.71; H, 7.79; N, 2.55. Single colorless crystals were grown from a CH_2Cl_2 solution at −30 °C: mp 136 °C. **7**: Carbodiimide **7** was characterized in solution (40% spectroscopic yield): ^{1}H NMR (C_6D_6) δ −0.15 (s, 1 H, C*H*SiCH$_3$), 0.09, 0.36 (s, 18 H, SiC*H*$_3$), 0.42 (s, $J_{^{117}SnH}$ = 47.7 Hz, $J_{^{119}SnH}$ = 50.0 Hz, 9 H, SnC*H*$_3$), 1.16 (m, 21 H, SiC*H*CH$_3$), 1.82 (broad s, 15 H, CpC*H*$_3$); ^{13}C NMR (C_6D_6) δ −5.94 (s, $J_{^{117}SnC}$ = 257.1 Hz, $J_{^{119}SnC}$ = 268.5 Hz, SnCH$_3$) 3.65, 4.33 (s, SiCH$_3$), 13.00 (broad s, CpCH$_3$), 13.51 (s, SiCHCH$_3$), 18.79 (s, SiCHCH$_3$), 126.41 (s, NCN), 136.10 (broad s, Cp), CHSiCH$_3$ was not observed, probably hidden by SiCH$_3$; ^{119}Sn NMR (C_6D_6) δ −64.46; IR (toluene, ν (cm^{-1})) 2162 (CNN); ^{14}N NMR (C_6D_6) δ −365 ($\nu_{1/2}$ = 390 Hz, NCN).

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